



Short Communication

Conversion of kraft lignin under hydrothermal conditions



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HIGHLIGHTS

- Hydrothermal treatment of kraft lignin.
- Maximum value of total oil yield (11% of kraft lignin).
- Main compounds of oils.
- Guaiacol amount (78% of oil) at 130 °C/60 min.
- Conversion mechanism is reported using GPC and FTIR.

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ABSTRACT

The aim of this study is to explore hydrothermal conversion of kraft lignin for value-added products. With ranging between 5.4% and 10.6%, total oil yield decreased with the increase of temperature (130, 180, and 230 °C), the longer reaction time (15–60 min) led to increased total oil yield. Main compound of oils characterized by GC–MS was guaiacol (2-methoxy phenol) in the range of 19–78% of oil depending on different reaction conditions. Residual kraft lignins were characterized by GPC and FTIR with respect to the conversion mechanism of kraft lignin by this process. The conversion of kraft lignin under hydrothermal conditions had something to do with the degradation of β -O-4 linkages, hydroxyl groups, carbonyl groups, aromatic rings resulting in the increased amount of phenolic OH groups in kraft lignin.

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1. Introduction

Lignin is a complex three-dimensional phenyl-propanoid polyphenol linked by ether bonds or carbon–carbon linkages as well as different functional groups. Kraft lignin is obtained as by-product from black liquor during kraft pulping which is by far the dominant chemical pulping process. However, the main use of kraft lignin is as a low-grade energy source in combustion and has not received much attention until recently (dos Santos et al., 2014). After separation from black liquor, some increasing applications of kraft lignin will be available in addition to the ones coming from the pulp industry. At the same time, due to the extreme complexity of lignin, novel processing methods and product concepts are required to increase utilization of kraft lignin as a raw material for higher value materials production (Long et al., 2014).

The conversion of biomass into value-added products is mostly performed using thermochemical processes, and very little attention is typically focused on kraft lignin. The thermochemical processes include three sub-categories: gasification (>600 °C), pyrolysis (370–530 °C, 0.1–0.5 MPa) and liquefaction (230–330 °C, 5–20 MPa) (Joffres et al., 2013). Pyrolysis is a classical route to obtain bio-oils from biomass. However the decomposition is complex and tar formation is observed. By using catalysts, the pyrolytic oil yield is increased and the composition is modified, but the continuous pyrolysis remains a technical challenge when applied to lignin (Li et al., 2012). Hydrothermal process has become an important process in the chemical conversion of biomass as water is a unique, and environmentally benign solvent. Karagöz et al. (2004) studied the possibility of low-temperature hydrothermal liquefaction of biomass. Murnieks et al. (2014) carried out hydro-treating of wheat straw in toluene and ethanol in order to obtain bio-components which are useful for fuel purposes.

It needs to be noted that even if there have been many reports on utilizing biomass using hydrothermal methods to produce liquid fuel or chemical feedstock, it remains a challenging task to

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convert and analyze kraft lignin under hydrothermal conditions. In the present paper, we attempted to investigate the conversion of kraft lignin from bamboo kraft pulping under hydrothermal conditions. The effects of reaction temperature and reaction time on yield of various products were investigated. The chemical compositions of the resulting oils were characterized using GC–MS. In addition, chemical information of kraft lignin and residual kraft lignin was examined by GPC and FTIR to further understand the conversion mechanism of kraft lignin.

2. Methods

2.1. Materials

All starting materials described herein were commercially purchased from Sinopharm Chemical Reagent Co., Shanghai (China) and used as received without further purification, unless otherwise noted. The kraft lignin was received from bamboo (*Dendrocalamus brandisii*, 27.1% lignin) cooking using NaOH and Na₂S by the conventional laboratory-scale kraft method. After cooking, black liquors were collected from the reaction vessel. Next DTPA was slowly added with agitation to black liquor to facilitate metal-ion removal followed by the addition of 2 M sulfuric acid until a pH of between 2 and 3 was reached causing some of the lignin to precipitate. The solution and resulting precipitate was kept at 0 °C overnight and thawed at room temperature. The precipitate was separated by centrifugation, then freeze dried and kept frozen until purification. The initial sample was heated in 80% dioxane containing 0.05 M HCl at reflux for 2 h in a nitrogen atmosphere, filtered through a medium sintered glass funnel at 0 °C, and sequentially washed up with 80% dioxane. All filtrates were collected, neutralized with solid NaHCO₃, and then evaporated under reduced pressure. The liquid after rotary evaporation was slowly added to the acidic distilled water (pH 2), lignin precipitate was centrifuged and freeze-dried. The lignin sample obtained was washed with methylene chloride (3 × 150 mL) and dried under vacuum with phosphorus pentoxide to give pure kraft lignin. The kraft lignin sample designated as BKL was stored in the refrigerator for testing. The acid insoluble (klason lignin) of kraft lignin was determined by the klason hydrolysis as described by Crawford and Pometto. The soluble lignin of kraft lignin was determined by measuring the absorbance of the hydrolyzate at 205 nm using Shimadzu UV–vis 160 spectrophotometer. Five milliliters of the same filtrate obtained was used to determine the carbohydrate content (3.38%) by applying the same spectrophotometer at 500 nm using 10–1000 g/mL glucose (Sigma, 99.9%) as standard (Crawford and Pometto, 1988). The purity of kraft lignin (BKL 91%) was calculated from the sum of acid insoluble and soluble lignin results. The ash content of kraft lignin (5.35%) was measured by the weight difference when kraft lignin was totally burned in muffle at a temperature of 575 °C in air. The energy content of the kraft lignin (24.32 kJ/g) was analyzed using a KSLR-400C calorimeter. Molecular weight of acetylated lignins was determined with Waters 2695 GPC gel permeation chromatography equipped with a differential refractive index detector using tetrahydrofuran (THF) as the eluent (1.00 mL/min). Acetylation was carried out in pyridine with acetic anhydride according to the published method (Samuel et al., 2010). A Vario EL III elemental analyzer was used to determine the elemental content of kraft lignin (65.28% C; 5.69% H; 0.39% N; 28.64% O).

2.2. Hydrothermal treatment of kraft lignin

The experiments were performed in a 250 mL SLM microreactor (Shanghai Laboratory Instrument Works Co., Ltd., China) equipped

with a magnetic stirrer and a SLM temperature controller. Typically, 5.0 g of kraft lignin and 30 mL of DI water were transferred into the reactor. The system was vented with nitrogen three times before each experiment to remove air from the reactor. For each experiment the reactor was heated in 30 min from ambient to a working temperature of 130 °C or 180 °C or 230 °C, after which the experiment was continued for 15 min or 60 min. The accuracy of the temperature controller was set at ±1 °C. The content was stirred continuously at 100 rpm during the hydrothermal treatment. At the end of the experiment, the gas was removed from the reactor after the autoclave was cooled down to room temperature with water. Thereafter, the content was taken and the reactor was thoroughly rinsed with DI water. The content was adjusted to pH 1–2 with 1.7 M HCl, filtered using a folded filter paper and washed with DI water of 100 mL. The residual kraft lignin obtained after filtering and washing was vacuum-dried. The liquid was extracted using equal amount of diethyl ether to obtain diethyl ether phase. The water phase separated from the extraction was extracted using equal amount of ethyl acetate to obtain ethyl acetate phase. The organic phases were dried with anhydrous sodium sulfate, filtered and finally vacuum-dried to obtain oil1 (diethyl ether phase) and oil2 (ethyl acetate phase). Each individual experiment was carried at least 3 times. The conversion and yield of various product were calculated on a dry basis using the following equation:

$$\text{Conversion (wt\%)} = \frac{m_{\text{kraft lignin}} - m_{\text{residue}}}{m_{\text{kraft lignin}}} \times 100;$$

$$\text{Oil yield (wt\%)} = \frac{m_{\text{oil}}}{m_{\text{kraft lignin}}} \times 100$$

$$\text{Gas yield (wt\%)} = \frac{m_{\text{(kraft lignin+water)}} - m_r}{m_{\text{(kraft lignin+water)}}} \times 100;$$

$$\text{Residue yield (wt\%)} = \frac{m_{\text{residue}}}{m_{\text{kraft lignin}}} \times 100$$

$$\text{Other (wt\%)} = 100 - (\text{oil1} + \text{oil2} + \text{residue} + \text{gas})$$

where $m_{\text{kraft lignin}}$ = mass of kraft lignin, m_{residue} = mass of residual kraft lignin, m_{oil} = mass of oil, $m_{\text{(kraft + water)}}$ = charged mass of kraft lignin and water, and m_r = recovered mass of products.

2.3. FTIR measurements

FTIR spectral measurements were done with a Bruker Tensor 27 spectrophotometer in the 4000–400 cm⁻¹ wavenumber range at a resolution of 2 cm⁻¹ wavelength, by averaging 20 scans.

2.4. GC–MS analysis of oils

The chemical composition of oil including oil1, oil2 obtained from hydrothermal liquefaction of kraft lignin was quantitatively analyzed with external standards by gas chromatograph equipped with a mass selective detector (Agilent HP6890-5973 GC–MS; quartz capillary column, 30 m × 0.25 mm × 0.25 μm). Temperature program: 40 °C (hold 10 min) → 280 °C (rate 10 °C/min) hold for 5 min. Compounds were identified by means of the Wiley library-HP G1035A and NIST library of mass spectra and subsets-HP G1033A.

3. Results and discussion

3.1. Yield

Experimental conditions, conversion, and yields are shown in Table 1. It is observed that temperature and time affected both product composition and yield of products. With an increase in the temperature from 130 °C (15 min, 60 min) to 180 °C (15 min, 60 min), total oil yield decreased from (7.4, 10.6) to (6.3,

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